

Anomalous Low Temperature States in CeNi₂Ge₂

F. M. Grosche*, P. Agarwal, S. R. Julian, N. J. Wilson, R. K. W. Haselwimmer,
S. J. S. Lister, N. D. Mathur, F. V. Carter, S. S. Saxena and G. G. Lonzarich
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK
(February 1, 2008)

Ambient pressure studies on high purity single crystals of the stoichiometric 4f-electron metal CeNi₂Ge₂ reveal anomalous low temperature forms of the resistivity which challenge our understanding of the metallic state. Comparisons are made with the isostructural and isoelectronic compound CePd₂Si₂ near the border of magnetism at high pressure, and possible reasons for this novel non-Fermi liquid form of the resistivity are discussed. Phase diagrams of further anomalies are presented, which involve a loss of resistance at low temperature in some samples of CeNi₂Ge₂ and unexpected high pressure phases.

74.20.Mn, 71.27.+a

I. INTRODUCTION

Strongly correlated electron materials in general and the heavy fermion compounds in particular exhibit unusual metallic states and low temperature phase transitions that remain only partly understood. The temperature dependences of the thermodynamic and transport properties, and in particular of the resistivity, allow us to identify a number of apparently distinct regimes. At high temperatures, a weakly temperature dependent, large resistivity consistent with scattering from thermally disordered local magnetic moments is observed down to an upper temperature scale, T_{sf} . Below T_{sf} , the resistivity drops with decreasing temperature and in the absence of a phase transition the resistivity and other bulk properties follow the predictions of Fermi liquid theory below a lower temperature scale T_{FL} . The range between T_{FL} and T_{sf} , sometimes described as a spin liquid regime, appears as a narrow cross-over region in most materials.

An increasing number of systems are coming to light, however, in which - due to their proximity to magnetic phase transitions - the Fermi liquid regime is suppressed to very low temperatures or even masked by the onset of superconductivity or other forms of order (see e.g. [1]). The unconventional normal states observed in these metals might be examined in the first instance in terms of phenomenological models for the fluctuations of the local order parameter, i.e. the local magnetisation for ferromagnetism and the local staggered magnetisation for antiferromagnetism [2], or of some associated variable. If the magnetic ordering temperature is suppressed to absolute zero, these modes soften over large portions of reciprocal space at low temperatures, leading to a strong enhancement of the quasiparticle scattering rate and potentially to a breakdown of the Fermi liquid description in its simplest form. This breakdown may be expected to be particularly apparent in the temperature dependence of the resistivity $\rho(T)$ that may deviate from the usual Fermi liquid form $\rho(T) \sim T^2$ in pure samples at low temperatures.

To look for a breakdown of the Fermi liquid description in pure materials as opposed to the more extensively studied doped [3,4] heavy fermion systems, we have selected stoichiometric compounds that are close to being magnetically ordered at low temperature and have used hydrostatic pressure to tune these compounds through quantum ($T \rightarrow 0K$) phase transitions.

The systems that we have selected, namely the isostructural and isoelectronic relatives CePd₂Si₂ and CeNi₂Ge₂, allow for examinations of an antiferromagnetic quantum critical point in pure metals for the first time in considerable detail. CeNi₂Ge₂ and CePd₂Si₂ are isostructural to the heavy fermion superconductor CeCu₂Si₂ [5] and its larger volume relative CeCu₂Ge₂ [6] (both with the ThCr₂Si₂ structure), but differ from CeCu₂Si₂ in the number of d electrons in the d-metal constituent, and hence in the character of the Fermi surface and in the magnetic properties.

At ambient pressure, CePd₂Si₂ orders in an antiferromagnetic structure with a comparatively small moment of $0.7 \mu_B$ below a Néel temperature T_N of about 10 K [7], which falls with increasing pressure [8]. The spin configuration consists of ferromagnetic (110) planes with spins normal to the planes and alternating in direction along the spin axis. In a recent study [9], we have elucidated the phase diagram of CePd₂Si₂ up to hydrostatic pressures of about 30 kbar. The Néel temperature has been found to drop linearly with pressure above 15 kbar and to extrapolate to zero at a critical pressure, $p_c \simeq 28$ kbar, while the shoulder in the resistivity, T_{sf} , shifts from 10 K at low pressure to about 100 K near p_c . Superconductivity appears below 430 mK in a limited pressure region of a few kbar on either side of p_c . This behaviour, and perhaps that in a related system CeRh₂Si₂ [10], is believed to be consistent with an anisotropic pairing arising from magnetic interactions [11,12]. Here, we concentrate on the striking normal state behaviour of the resistivity, which deviates strongly from the T^2 form usually associated with a Fermi-liquid (upper curve in Fig. 1 and left inset in Fig. 2). The range between T_{sf} and T_{FL} , in many materials a narrow cross-over regime, thus appears to open

up to more than two orders of magnitude in temperature and becomes the dominant feature of the system, exposing the intervening spin liquid state for closer scrutiny.

The electronically and structurally equivalent compound CeNi_2Ge_2 [13], which is of central interest here, has a slightly smaller lattice constant and its zero pressure behaviour may be expected to be similar to that of CePd_2Si_2 at a pressure close to but higher than p_c .

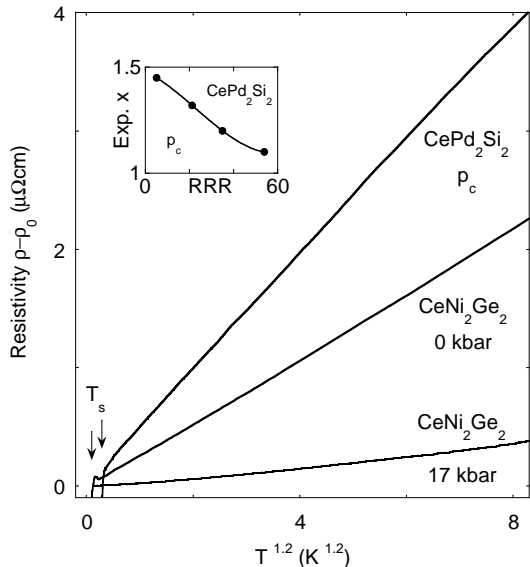


FIG. 1. Low temperature resistivity plotted against $T^{1.2}$ (i) in CeNi_2Ge_2 at ambient pressure (denoted everywhere as 0 kbar) and at high pressure (17 kbar), and (ii) in CePd_2Si_2 near the critical pressure $p_c \simeq 28$ kbar, where $T_N \rightarrow 0$ K. For comparison, the curves are shifted by their respective $T = 0$ intercepts, i.e. their residual resistivities, ρ_0 . For CeNi_2Ge_2 , $\rho_0 \simeq 0.27 \mu\Omega\text{cm}$ at $p = 0$ and $\simeq 0.23 \mu\Omega\text{cm}$ at 17 kbar, while for CePd_2Si_2 , $\rho_0 \simeq 1.9 \mu\Omega\text{cm}$ at 28 kbar. Inset: The resistivity exponent x , defined by fitting $\rho(T) = \rho_0 + AT^x$ from 0.4 K to 4 K for a number of samples of CePd_2Si_2 of varying residual resistivity ratio, $\text{RRR} = \rho(293\text{K})/\rho_0$. Samples with the highest RRR were produced in an RF furnace by quenching a high purity stoichiometric melt in a water cooled copper boat in UHV or ultra pure argon atmosphere. The ingots were then annealed at approximately 100 °C below the melting temperature for one day. Samples with RRR of over 50 for CePd_2Si_2 and 300 for CeNi_2Ge_2 were thus obtained.

II. RESULTS

As shown in Fig. 1, high purity samples of CeNi_2Ge_2 at ambient pressure and of CePd_2Si_2 at p_c exhibit qualitatively similar anomalous temperature dependences of the resistivity.

For CePd_2Si_2 near p_c , the resistivity has a form $\rho = \rho_0 + AT^x$ with an exponent x close to 1 over a wide range, from the onset of superconductivity near 0.4 K up to about 40 K (left inset of Fig. 2). Experiments carried out

on various samples and different sample orientations have revealed a variation of the exponents in the range $1.1 < x < 1.4$ and a general trend towards lower values for purer (lower ρ_0) specimens, indicating a possible limiting value of close to 1 for ideally pure samples (inset of Fig. 1).

Our present measurements at ambient pressure show that CeNi_2Ge_2 follows a similar power law variation of the resistivity over at least an order of magnitude in temperature above about 200 mK and up to pressures of at least 17 kbar (Fig. 1). We have extended this study to lower temperatures under applied magnetic fields in a high quality sample, which showed no sign of a superconducting transition down to 100 mK at 0.5 T and above. At 0.5 T, a detailed analysis of the temperature dependence of the power-law exponent (more precisely, the logarithmic derivative defined in the caption of Fig. 2) reveals a rapid cross-over to the Fermi-liquid value $x = 2$ below a temperature $T_{FL} \simeq 200$ mK (Fig. 2). This cross-over region rises and broadens with increasing magnetic field (Fig. 2).

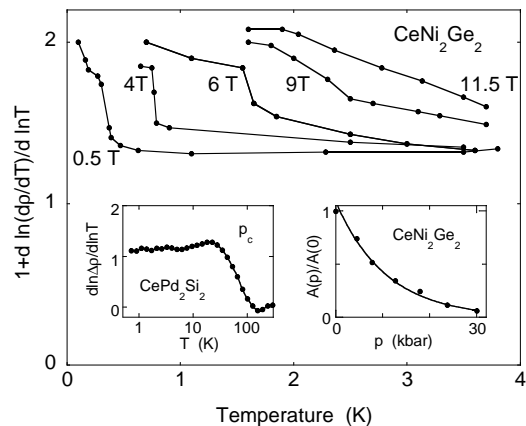


FIG. 2. High sensitivity measurement of the logarithmic derivative $(1 + d \ln(d\rho/dT)/d \ln T)$ of the resistivity $\rho(T)$ in CeNi_2Ge_2 at ambient pressure and in applied magnetic fields. The ordinate reduces to the resistivity exponent x where $\rho(T)$ can be expressed in the form $\rho(T) = \rho_0 + AT^x$. The resistivity was measured along the a -axis with the magnetic field applied along the c -axis. The residual resistivity of the sample was approximately $0.7 \mu\Omega\text{cm}$. Left inset: The temperature dependence of $d \ln(\Delta\rho = \rho - \rho_0)/d \ln T$ vs. T for CePd_2Si_2 close to p_c . The ordinate again reduces to the resistivity exponent x under the condition given above. In contrast to $(1 + d \ln(d\rho/dT)/d \ln T)$, $d \ln(\Delta\rho)/d \ln T$ is not independent of the method of determining the residual resistivity. For reasonable estimates of ρ_0 , however, the two expressions yield the same result to ± 0.1 over most of the temperature range explored. Right inset: Pressure-dependence of the coefficient A , obtained by fitting the resistivity of CeNi_2Ge_2 to the power-law $\rho = \rho_0 + AT^x$ from 0.4 K to 10 K.

These findings indicate that CeNi_2Ge_2 is delicately

placed close to the critical point studied in CePd_2Si_2 at high pressure, returning to Fermi liquid behaviour at low temperatures as the spin fluctuations are quenched by an increasing magnetic field.

One sample of CeNi_2Ge_2 shows a complete loss of resistance at ambient pressure below 200 mK (Fig. 3), similar to the occurrence of superconductivity in high pressure CePd_2Si_2 , while a number of other high quality crystals exhibit a drop in $\rho(T)$ of about 85% at low temperatures. We note that a downturn of approximately 10% in the resistivity of CeNi_2Ge_2 below 100 mK is also evident from data in [14]. A study of the shift of this transition in a second sample with magnetic field yields an initial slope $dB_{c2}/dT \simeq -5\text{ T/K}$ (inset of Fig. 3), comparable with the value of $\simeq -6\text{ T/K}$ observed for the superconducting transition in high-pressure CePd_2Si_2 [15]. The transition is very sensitive to hydrostatic pressure (inset of Fig. 3) and above 4 kbar, no drop of the resistivity is observed. The resulting phase diagram is reminiscent of the behaviour of CePd_2Si_2 at high pressure and is consistent with our conjecture that CeNi_2Ge_2 is a smaller volume relative of CePd_2Si_2 .

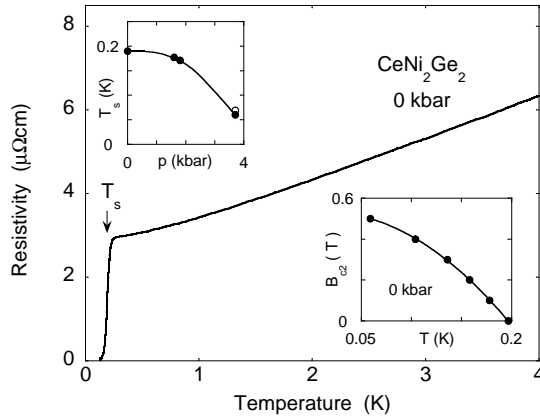


FIG. 3. Low temperature resistivity $\rho(T)$ in CeNi_2Ge_2 at ambient pressure in a sample which exhibits a complete loss of resistance below 200 mK. Upper inset: The variation of the transition temperature T_s with hydrostatic pressure. T_s is measured at the 50% drop in $\rho(T)$ (solid points), except at the highest pressure where the drop in resistivity is 14% (open point) at the lowest temperature reached (the solid point in this case was obtained by extrapolation). No significant drop in resistance was observed above 4 kbar. Lower inset: Magnetic field dependence of the transition temperature T_s in another sample of CeNi_2Ge_2 , indicating an initial slope $dB_{c2}/dT \simeq -5\text{ T/K}$.

Further anomalies were discovered at still higher pressure in CeNi_2Ge_2 , which showed indications of a new ordered phase (labelled T_x in Fig. 4) at around 1 K and, again, a drop of resistance of up to 100% below about 0.4 K (T_s in Fig. 4), reminiscent of superconductivity. We note that early measurements of the specific heat in

the same region of the phase diagram have revealed an anomalous peak, which may be associated with our upper transition at T_x [16]. In contrast to the superconducting phase found in high pressure CePd_2Si_2 and to the corresponding low pressure phase in CeNi_2Ge_2 , these high pressure states in CeNi_2Ge_2 are relatively insensitive to variations of lattice density. In this sense they are reminiscent of the behaviour observed in CeCu_2Si_2 , where a superconducting phase persists over a wide region of pressure up to about 100 kbar [17].

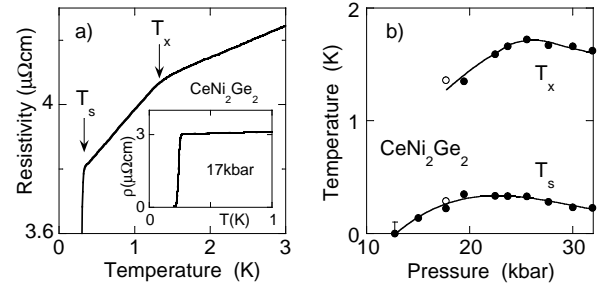


FIG. 4. Further high pressure phases in CeNi_2Ge_2 can be identified from anomalies in the form of $\rho(T)$ at low temperature. (a): Low temperature resistivity of a sample of CeNi_2Ge_2 . T_s labels a sudden loss in resistance, which is complete in a number of samples (inset), while T_x refers to a kink in the temperature dependence of $\rho(T)$ reminiscent of a magnetic phase transition. (b): Pressure dependence of the two anomalies determined on a second sample (closed symbols) and the data extracted from (a) (open symbols). These high pressure transitions are most pronounced in samples of CeNi_2Ge_2 produced by slow Czochralski pulling from a pure stoichiometric melt in a water cooled Cu boat. Crystals grown in this way were found to have values of RRR of around 20.

III. DISCUSSION

In both CeNi_2Ge_2 and CePd_2Si_2 , the temperature dependence of the resistivity is characterised over a wide range by a power-law with exponent close to 1, and by rapid cross-overs to the high and low temperature forms. This behaviour is not limited to a critical lattice density alone, but, at least in CeNi_2Ge_2 , appears to extend over a considerable range in pressure. These properties of our two tetragonal metals contrast sharply with that of the cubic antiferromagnet CeIn_3 [18,12]. In the latter the resistivity deviates from the Fermi liquid form only in a very narrow pressure range near the critical pressure p_c where $T_N \rightarrow 0\text{ K}$. At p_c and in low magnetic fields the resistivity exponent, or more precisely $d\ln(\rho - \rho_0)/d\ln T$, grows smoothly with decreasing temperature and tends towards a value of about 3/2 at around 1 K.

We now consider to what extent these findings may be understood in terms of the standard model for spin fluctuation scattering. In this model, the resistivity is given essentially by the population of spin excitations

that is proportional to an effective volume q_T^d in reciprocal space centred on the ordering wavevector \mathbf{Q} . Here d is the spatial dimension and q_T is a characteristic thermal wavevector that is proportional to $T^{1/z}$, if the spin fluctuation rate $\Gamma_{\mathbf{Q}+\mathbf{q}}$ at a wavevector $\mathbf{Q} + \mathbf{q}$ varies as q^z at a small q and at p_c . For the simplest case, $z = 2$ and thus the resistivity is predicted to vary as T for $d = 2$ and $T^{3/2}$ for $d = 3$ far below T_{sf} and at p_c , when antiferromagnetic order vanishes continuously [2]. These results are qualitatively consistent with experiment, if we take $d = 3$ for cubic CeIn_3 , and if the effective dimension is closer to 2 for tetragonal CePd_2Si_2 and CeNi_2Ge_2 . The latter assumption is not necessarily inconsistent with the known magnetic structure of CePd_2Si_2 , that suggests a frustrated spin coupling along the c -axis and hence a strongly anisotropic spin fluctuation spectrum [15,12].

There are at least two major difficulties with this description. Firstly, it assumes that essentially all carriers on the Fermi surface scatter strongly from excited spin fluctuations. This assumption, however, cannot be justified within the usual Born approximation in the presence of harmonic spin fluctuations in an ideally pure system. Under these conditions, those carriers not satisfying the ‘Bragg’ condition for scattering from critical spin fluctuations near \mathbf{Q} are only weakly perturbed and at low T lead to a Fermi liquid T^2 resistivity and *not* to the above anomalous exponents [19]. Secondly, for the standard form assumed for the temperature and pressure dependence of $\Gamma_{\mathbf{Q}+\mathbf{q}}$ the model of the last paragraph predicts (i) a gradual increase of $d \ln \rho / d \ln T$ with decreasing T tending to the limiting exponent only for $T \ll T_{sf}$, and (ii) a rapid cross-over to the Fermi liquid exponent at low T as a function of pressure (or when the magnetic transition is not continuous). Neither of these predictions appear to be consistent with our findings in CePd_2Si_2 and CeNi_2Ge_2 .

The first of these two difficulties may perhaps be cured by including the effects of residual impurities, spin fluctuation anharmonicity, and corrections to the Born approximation that may homogenise the quasiparticle relaxation rate over the Fermi surface. The second problem might be resolved by means of a more realistic model for the temperature and pressure dependences of $\Gamma_{\mathbf{Q}+\mathbf{q}}$ than that currently employed. A first step towards such refinements has recently been proposed, specifically for the effects of residual impurities [20], but it is too early to tell whether or not it can account for all of the features we observe, both in our tetragonal and the cubic systems, in a consistent way.

We also point out that a description of CePd_2Si_2 and CeNi_2Ge_2 based on a more extreme separation of charge and spin degrees of freedom than is present in current approaches, cannot be ruled out [21]. A complete theory would have to account not only for the differences between our tetragonal and cubic systems and the unexpectedly wide range of apparent criticality in CePd_2Si_2 and CeNi_2Ge_2 , but also for the occurrence of superconductivity on the border of antiferromagnetism in all of

these cases, and the higher pressure phases that we observe in CeNi_2Ge_2 .

IV. CONCLUSION

The 4f-electron metals CeNi_2Ge_2 and CePd_2Si_2 offer the possibility of observing an unconventional normal state over a wide window in temperature and pressure without chemical doping. The similarity between the two materials suggests that CeNi_2Ge_2 at ambient pressure is conveniently placed very close to the antiferromagnetic quantum critical point, as studied under high pressure in CePd_2Si_2 , and make it an attractive material for future investigations. The fixed value of the power-law exponents over a wide range in temperature - reminiscent of the behaviour observed in some of the high T_c oxides - and the wide pressure range of apparent criticality appear to defy a description in terms of the spin fluctuation model in its simplest form.

Superconductivity in rare-earth based heavy fermion metals is an uncommon phenomenon. CeNi_2Ge_2 may be the second ambient pressure superconductor in this class after CeCu_2Si_2 , if the zero-resistance state observed at low pressures can be identified as superconductivity. The pairing mechanism in CePd_2Si_2 and CeNi_2Ge_2 , in which superconductivity exists only close to the very edge of antiferromagnetic order, may however be different from that in CeCu_2Si_2 [22]. On the other hand, the high pressure, zero-resistance state in CeNi_2Ge_2 could offer a new perspective for our understanding of the first heavy fermion superconductor, CeCu_2Si_2 .

ACKNOWLEDGMENTS

We thank, in particular, P. Coleman, J. Flouquet, P. Gegenwart, C. Geibel, I. Gray, S. Kambe, D. Khmel'nitskii, F. Kromer, M. Lang, A. P. Mackenzie, G. J. McMullan, A. J. Millis, P. Monthoux, C. Pfleiderer, A. Rosch, G. Sparn, F. Steglich, A. Tsvelik and I. R. Walker. The research has been supported partly by the Cambridge Research Centre in Superconductivity, headed by Y. Liang, by the EPSRC of the UK, by the EU, and by the Cambridge Newton Trust.

* New address: MPI-CPFS, Bayreuther Str. 40, D-01187 Dresden, Germany.

- [1] See, e.g. S. R. Julian, C. Pfleiderer, F. M. Grosche, N. D. Mathur, G. J. McMullan, A. J. Diver, I. R. Walker and G. G. Lonzarich, *J. Phys.: Cond. Matter* **8**, 9675 (1996).
- [2] T. Moriya and T. Takimoto, *J. Phys. Soc. Japan* **64**, 960 (1995); A. J. Millis, *Phys. Rev. B* **48**, 7183 (1993); G. G.

- Lonzarich, in *Electron*, edited by M. Springford (Cambridge University Press, Cambridge, England, 1997) and references cited therein.
- [3] Recent discussions may be found in the proceedings of the Santa Barbara ITP Meeting, J. Phys.: Cond. Matter **8** (1996).
 - [4] A. Rosch, A. Schröder, O. Stockert and H. v. Löhneysen, Phys. Rev. Lett. **79**, 159 (1997).
 - [5] F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and J. Schäfer, Phys. Rev. Lett. **43**, 1892 (1979).
 - [6] D. Jaccard, K. Behnia, and J. Sierro, Phys. Lett. A **163A**, 475 (1992).
 - [7] B. H. Grier, J. M. Lawrence, V. Murgai, and R. D. Parks, Phys. Rev. B **29**, 2664 (1984).
 - [8] J. D. Thompson, R. D. Parks, and H. Borges, JMMM **54-57**, 377 (1986).
 - [9] F. M. Grosche, S. R. Julian, N. D. Mathur, and G. G. Lonzarich, Physica B **223&224**, 50 (1996).
 - [10] R. Movshovich, T. Graf, D. Mandrus, J. D. Thompson, J. L. Smith, and Z. Fisk, Phys. Rev. B **53**, 8241 (1996).
 - [11] See, e.g., A. Millis, S. Sachdev, and C. M. Varma, Phys. Rev. B **37**, 4975 (1988).
 - [12] N. D. Mathur, F. M. Grosche, S. R. Julian, I. R. Walker, D. M. Freye, R. K. W. Haselwimmer and G. G. Lonzarich, Nature **394**, 39 (1998).
 - [13] G. Knopp *et al.*, J. Magn. Magn. Mat. **74**, 341 (1988); T. Fukuhara *et al.*, J. Magn. Magn. Mater. **140-144**, 889 (1995); F. Steglich *et al.*, Z. Phys. B **103**, 235 (1997); J. Flouquet, private communication (1997); S. J. S. Lister *et al.*, Z. Phys. B **103**, 263 (1997). See also [1].
 - [14] P. Gegenwart, F. Kromer, M. Lang, G. Sparn, C. Geibel and F. Steglich, preprint (1998).
 - [15] F. M. Grosche, N. J. Wilson, R. K. W. Haselwimmer, S. J. S. Lister, N. D. Mathur, S. R. Julian and G. G. Lonzarich, preprint, aps1997aug27_001 (1997).
 - [16] P. Hellmann, L. Donnevert, S. Thomas, C. Geibel, G. Sparn and F. Steglich, Czech. J. Phys. **46**, 2591 (1996).
 - [17] B. Bellarbi, A. Benoit, D. Jaccard, J. M. Mignot and H. F. Braun, Phys. Rev. B **30**, 1182 (1984).
 - [18] I. R. Walker, F. M. Grosche, D. M. Freye, and G. G. Lonzarich, Physica C **282**, 30 (1997).
 - [19] R. Hlubina and T. M. Rice, Phys. Rev. B **51**, 9253 (1995).
 - [20] A. Rosch, preprint, cond-mat/9810260 (1998).
 - [21] P. Coleman, preprint, cond-mat/9809436 (1998); A. Schröder, G. Aeppli, E. Bucher, R. Ramazashvili and P. Coleman, Phys. Rev. Lett. **80** 5623 (1998); P. W. Anderson in *Theory of Superconductivity of High- T_c Cuprate Superconductors* (Princeton University Press, 1997).
 - [22] H. Razafimandimby, P. Fulde, and J. Keller, Z. Phys. B **54**, 111 (1984).